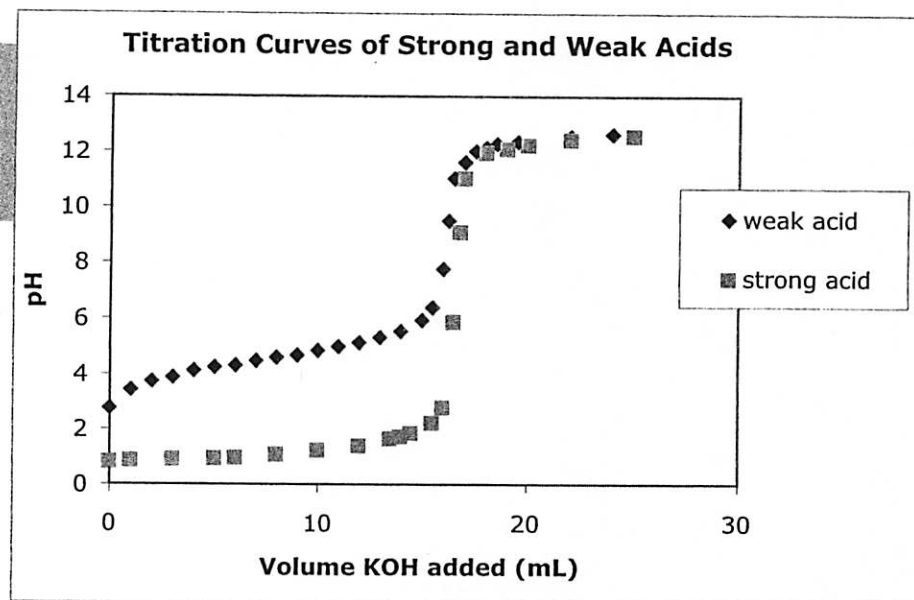


### Method III: Determining $K_a$ of a Weak Acid from a Titration Curve

The previous two methods work very well and quickly to determine the  $K_a$  of a weak monoprotic acid. But there is another method for determining the  $K_a$  of an acid, and this one also provides additional valuable information—such as how protic the acid is, and what indicator(s) will work to show the endpoint of a titration. This third method involves a titration, but in this case the pH of the resulting solution is recorded after each addition of a known volume of base. A graph of the pH on the y-axis, versus the total volume of base added on the x-axis, is called a **titration curve**. The shape of the curve tells whether the acid is strong or weak, as illustrated in Figure 10.1.

Figure 10.1  
Titration Curves  
of Strong  
and Weak Acids



If there is an initial rise in pH, after addition of a small amount of base, which levels off over a wide region before transitioning from an acidic pH to a basic pH, then the acid is a weak acid. A strong acid titration curve does not have this initial bump; rather, there is a gradual increase in pH before the transition to basic pH. Notice that these transitions occur when the pH changes extremely fast upon addition of an extremely small volume of base. It is for this reason that you add the base by the drop as you approach the endpoint of a titration using an indicator: because a few drops of base cause an extreme change in pH, the indicator will change color upon addition of one drop of base.

In addition, the shape of a titration curve tells whether the acid is mono-, di-, or triprotic. As Figures 10.2 and 10.3 show, if the titration curve contains one hump, the acid is monoprotic; if there are two humps on the curve, the acid is diprotic. A triprotic acid would have three humps.

It is likely that other acid-base titrations you have performed used an indicator to show the endpoint of the titration. It is the endpoint of the titration when the indicator undergoes a specific color change. It turns out that indicators change colors at specific pH values (see Experiment 11, on determining  $K_{in}$  of bromocresol green, for more information on how an indicator works), so when enough base has been added, the pH of the resulting solution will become more basic. When a certain pH is reached, the indicator will change color and the experimenter is trained to stop adding base at this point. We assume that this is the point where the acid has been completely neutralized by addition of the stoichiometric amount of base.

Figure 10.2  
Titration Curve  
of Monoprotic  
Acid

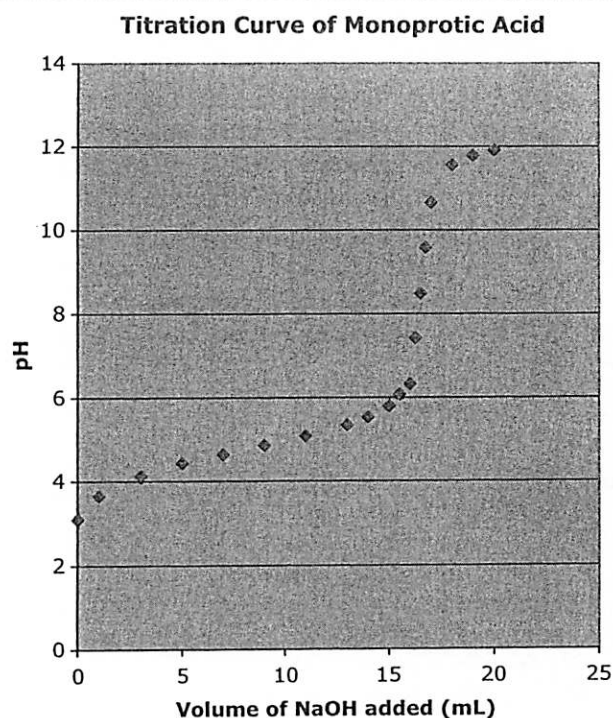
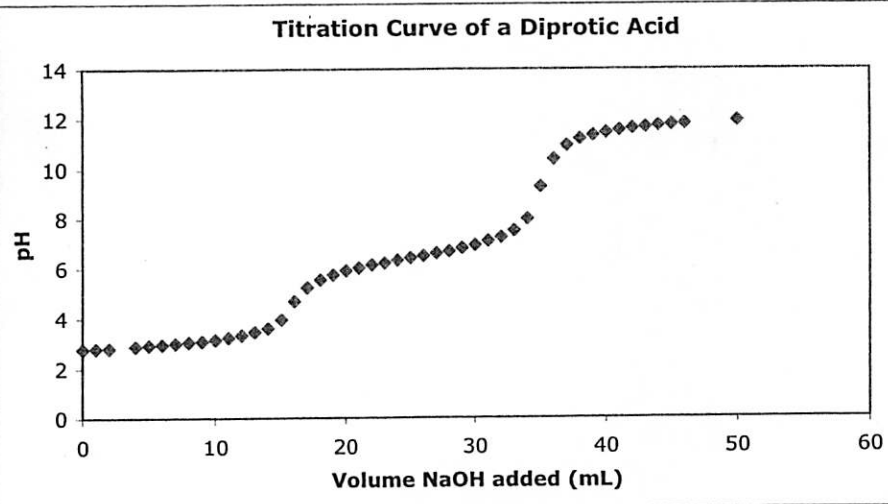


Figure 10.3  
Titration Curve  
of a Diprotic  
Acid



It turns out, however, that the endpoint may not be the true stoichiometric end of the reaction, but rather indicate the pH at which the indicator itself loses a proton, resulting in a color change. Did you ever wonder how one determines which indicator to use to do this? A titration curve can tell you. The true stoichiometric equivalence point can be determined by careful analysis of the titration curve, looking for the region on the curve where the concavity of the curve changes. The titration curve, then, shows the **equivalence point**, not the endpoint. At the equivalence point, all of the acid has reacted and converted into the conjugate base of the acid. The pH at the equivalence can be used to determine the indicator(s) that change colors a little past the pH at the equivalence point. *Note:* if it takes 25.00 mL of NaOH to reach the equivalence point during the titration of a weak monoprotic acid, it will take 12.50 mL to reach the 1/2-equivalence point, and this is a very important point on the titration, because at this point the concentration of the weak acid will equal the concentration of its conjugate base (because 1/2 of the acid has been neutralized). So, as demonstrated in Method II, when

$$[\text{HA}] = [\text{A}^-], \text{ then } K_a = [\text{H}^+]$$

and the pH equals the  $\text{p}K_a$  of the acid.

The pH of the solution changes very gradually around the 1/2-equivalence point when the base is added and the ratio of concentrations of [conjugate base]/[acid] is close to 1. This is called the buffer region of the titration curve, because this is where there is a mixture of the weak acid and its conjugate base in a ratio between 0.1 and 10.

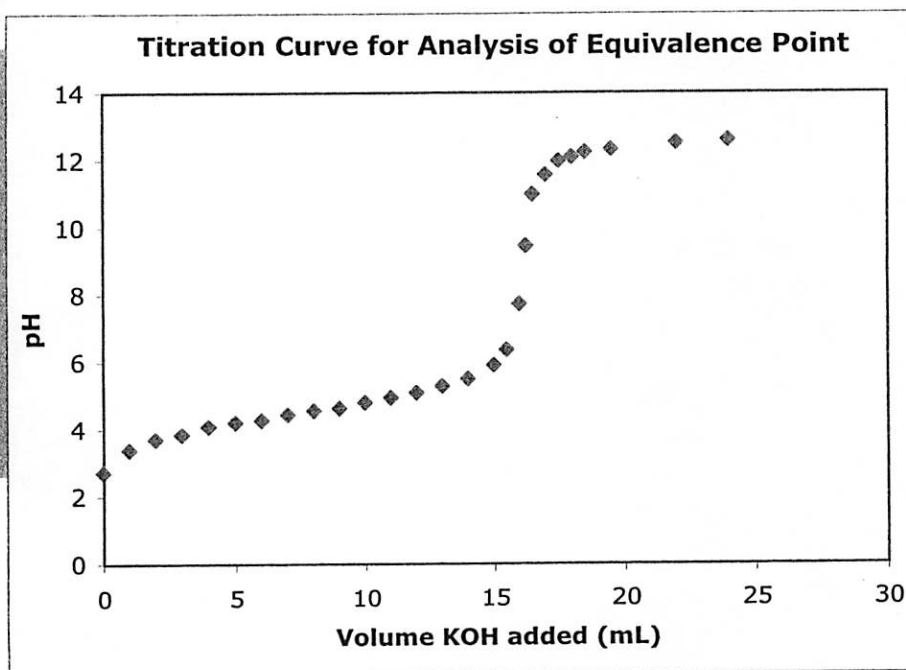
Clearly, the most important point to determine on a titration curve is the equivalence point, since from this the 1/2-equivalence point and  $K_a$  are calculated. If the acid is diprotic, there are two equivalence points, and the second equivalence point will show the more dramatic pH change and is easier to find and analyze. But, 1/2 the volume to the second is not a 1/2-equivalence point; rather, it is the first equivalence point. So, 1/4 the volume to the second equivalence point will give the volume of the first 1/2-equivalence point:

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}$$

The pH here equals  $pK_{a1}$ . The second 1/2-equivalence point is halfway between the first and second equivalence point, or 3/4 of the volume of the second equivalence point. The pH here will equal  $pK_{a2}$ . Also, the pH at the final equivalence point will tell you what indicator(s) will indicate the endpoint of the titration. It should go without saying, since the equivalence point tells you the volume of base added to neutralize the acid, and the shape of the titration curve tells you the reaction stoichiometry of the acid and base, that the titration curve allows for the most thorough analysis of an acid.

The equivalence point can be determined by following either the "circle method," "line method," or "right angle method." Equivalence point can also be found by taking the first or second derivative of the titration curve data. There now follow step-by-step approaches to determining the equivalence point using each of these methods. When studying the circle, line, or right-angle methods, refer to a copy of Figure 10.4, which it will be helpful for you to sketch in as you study the steps.

**Figure 10.4**  
Titration Curve for Analysis of Equivalence Point  
Various graphical methods may be used to determine the equivalence point for titration curves such as this one.



### Circle Method to Determine Equivalence Point(s) on Titration Curve

1. Graph the titration curve to determine whether it is of a mono- or diprotic acid. Find the transition area that occurs with the largest volume of base added. This area will have the steepest positive slope, where the pH change is greatest in respect to the least change in volume. This area will have the only (or second) equivalence point.

2. Fit two curved regions that bracket the transition from low to high pH, using circles that fit the natural curvature in each region. (Either a rubber stopper—with one hole if possible—or a beaker provide nice circle templates to use in this step. Find the correct-sized template by trying a variety of different-sized circles, then trace the one on the titration curve that touches the most data points.)
3. Find the center of each circle drawn in Step 2 and mark each center. (The center of a circle that was traced using a one-holed rubber stopper is the hole.)
4. Draw a line connecting the centers of these circles
5. The point where the line connecting the centers intersects the titration curve is the equivalence point.
6. Drop a perpendicular from this intersection point to the  $x$ -axis to determine the volume of base added to reach the equivalence point.
7. Calculate  $1/2$  this volume of base. This volume represents the  $1/2$ -equivalence point if the acid analyzed is a monoprotic acid; or, if the acid is a diprotic acid, the volume at the first equivalence point.

### Line Method to Determine Equivalence Point(s) on Titration Curve

1. Using a straightedge, draw a line of best fit for the first region on the titration curve where the pH is most stable.
2. Repeat Step 1, but do this for the region at the end of the titration curve.
3. Draw a best-fit line for the steep region on the titration curve where the pH change is greatest for the least change in volume.
4. Mark the two points where this steep line from Step 3 intersects each of the lines drawn in Steps 1 and 2.
5. Measure the distance between the two points marked in Step 4. Calculate the midpoint between these points and mark this point clearly.
6. Drop a perpendicular from this midpoint mark to the  $x$ -axis to determine the volume of base added to reach the equivalence point.
7. Calculate half this volume of base. This volume represents the half-equivalence point if the acid analyzed is a monoprotic acid, or, if the acid is a diprotic acid, the volume at the first equivalence point.

### Right-Angle Method to Determine Equivalence Point(s) on Titration Curve

1. Taking a T-square or other device with a true right angle, slide it along the  $x$ -axis until the curve goes vertical. This region indicates the equivalence point because it is the steepest part of the curve.
2. Calculate half of the so-indicated volume of base. This volume represents the half-equivalence point, if the acid analyzed is a monoprotic acid. If the acid is a diprotic acid, the volume represents the first equivalence point.

### Derivative Method to Determine Equivalence Point(s) on Titration Curve

Although some programs for the computer and calculator will calculate the first- and second-derivatives for you, finding derivatives can be done by hand or on a spreadsheet using the raw pH and volume data. The first derivative is the

$$\frac{\text{change in pH}}{\text{change in volume}} \text{ or } \frac{\Delta \text{pH}}{\Delta V}$$

that is, the slope of the line tangent to a given data point. To calculate this value, you must perform a series of identical calculations using sliding pairs of the volume and pH data. Because each calculation creates a new data point by using a pair of data points from the original pH and volume data, each derivative results in one fewer data points—that is, one data point lost per derivative taken. The data in Table 10.1 are taken from the titration of acetic acid; it

is the pH and volume of NaOH added for the region near the equivalence point that are given.

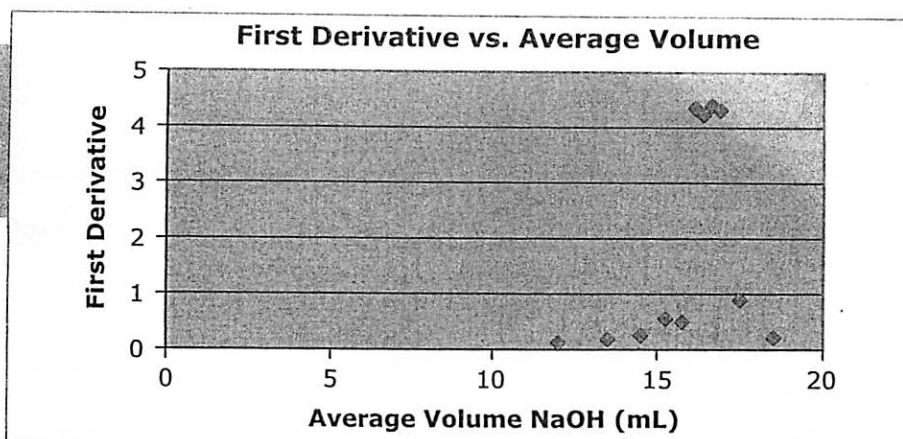
Following the table is a description of how to calculate the first derivative by hand. For clarity, only the data from the titration curve for acetic acid that brackets the equivalence point, not all the data points, are analyzed. However, first derivatives along the entire titration curve could be calculated using the method that is laid out. Note that the solutions to the equations set up in Columns 4 and 5 are shown in **bold**.

**Table 10.1**  
Data from  
Titration Curve  
and Calculation  
of First Derivative

Column 1	Column 2	Column 3	Column 4	Column 5
Sample #	Volume of NaOH (in mL)	pH	Average Volume (in mL)	$\frac{\Delta \text{pH}}{\Delta \text{Volume}}$ (First Derivative)
S1	11.00	5.11		
S2	13.00	5.37	(S2 + S1)/2 (13.00 + 11.00)/2 <b>12.00</b>	(pH <sub>2</sub> - pH <sub>1</sub> )/(V <sub>2</sub> - V <sub>1</sub> ) (5.37 - 5.11)/(13.00 - 11.00) <b>0.13</b>
S3	14.00	5.56	(S3 + S2)/2 (14.00 + 13.00)/2 <b>13.50</b>	(pH <sub>3</sub> - pH <sub>2</sub> )/(V <sub>3</sub> - V <sub>2</sub> ) (5.56 - 5.37)/(14.00 - 13.00) <b>0.19</b>
S4	15.00	5.82	(S4 + S3)/2 (15.00 + 14.00)/2 <b>14.50</b>	(pH <sub>4</sub> - pH <sub>3</sub> )/(V <sub>4</sub> - V <sub>3</sub> ) (5.82 - 5.56)/(15.00 - 14.00) <b>0.26</b>
S5	15.50	6.10	(S5 + S4)/2 (15.50 + 15.00)/2 <b>15.25</b>	(pH <sub>5</sub> - pH <sub>4</sub> )/(V <sub>5</sub> - V <sub>4</sub> ) (6.10 - 5.82)/(15.50 - 15.00) <b>0.56</b>
S6	16.00	6.35	(S6 + S5)/2 (16.00 + 15.50)/2 <b>15.75</b>	(pH <sub>6</sub> - pH <sub>5</sub> )/(V <sub>6</sub> - V <sub>5</sub> ) (6.35 - 6.10)/(16.00 - 15.50) <b>0.50</b>
S7	16.25	7.44	(S7 + S6)/2 (16.25 + 16.00)/2 <b>16.13</b>	(pH <sub>7</sub> - pH <sub>6</sub> )/(V <sub>7</sub> - V <sub>6</sub> ) (7.44 - 6.35)/(16.25 - 16.00) <b>4.36</b>
S8	16.50	8.50	(S8 + S7)/2 (16.50 + 16.25)/2 <b>16.38</b>	(pH <sub>8</sub> - pH <sub>7</sub> )/(V <sub>8</sub> - V <sub>7</sub> ) (8.50 - 7.44)/(16.50 - 16.25) <b>4.24</b>
S9	16.75	9.60	(S9 + S8)/2 (16.75 + 16.50)/2 <b>16.63</b>	(pH <sub>9</sub> - pH <sub>8</sub> )/(V <sub>9</sub> - V <sub>8</sub> ) (9.60 - 8.50)/(16.75 - 16.50) <b>4.40</b>
S10	17.00	10.68	(S10 + S9)/2 (17.00 + 16.75)/2 <b>16.88</b>	(pH <sub>10</sub> - pH <sub>9</sub> )/(V <sub>10</sub> - V <sub>9</sub> ) (10.68 - 9.60)/(17.00 - 16.75) <b>4.32</b>
S11	18.00	11.58	(S11 + S10)/2 (18.00 + 17.00)/2 <b>17.50</b>	(pH <sub>11</sub> - pH <sub>10</sub> )/(V <sub>11</sub> - V <sub>10</sub> ) (11.58 - 10.68)/(18.00 - 17.00) <b>0.90</b>
S12	19.00	11.80	(S12 + S11)/2 (19.00 + 18.00)/2 <b>18.50</b>	(pH <sub>12</sub> - pH <sub>11</sub> )/(V <sub>12</sub> - V <sub>11</sub> ) (11.80 - 11.58)/(19.00 - 18.00) <b>0.22</b>

The data are analyzed in pairs, with the average of the volumes taken first, using sequential sliding pairs of volumes, as shown in Column 4. Then the first derivative ( $\Delta \text{pH} / \Delta \text{Volume}$ ) is calculated, also using sequential sliding pairs, as shown in Column 5. Now the first derivative of the titration curve graph may be graphed, as shown in Figure 10.5, where the first derivative data from Column 5 are plotted on the y-axis versus the average volume data on the x-axis.

**Figure 10.5**  
First Derivative  
vs.  
Average Volume

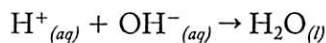


The volume at the equivalence point is determined from this graph by dropping a perpendicular to the  $x$ -axis from the maximum  $y$  value, as this is the point where the slope changes from positive to negative, a characteristic of the point where the concavity of the titration curve changes.

The second derivative can then be calculated by the same process as for the first derivative, using sliding sequential pairs. But instead of analyzing the pH and volume data, the data of average volume (Column 4) and the first derivative data (Column 5) are used. Again, you will end up with one fewer data point.

The reaction between a weak acid and a strong base may be modeled as a three-step process:

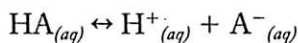
#### Step 1 Reaction between the hydrated proton and hydroxide ion



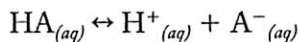
The number of moles of proton that react with the base is determined by the limiting reactant.

#### Step 2 Replacement of reacted hydrated proton by ionization of more weak acid

As the concentration of hydrated proton decreases when it reacts with the hydroxide ion, more of the unionized weak acid, HA, ionizes to replace the reacted  $\text{H}^+_{(aq)}$ . This can be thought of as an application of Le Chatelier's Principle.



#### Step 3 Reestablishment of equilibrium between weak acid and its conjugate base



As more base is added, Steps 1 and 2 continue until all the added hydroxide ion, which is the limiting reactant, reacts, leaving only HA and  $\text{A}^-$  in solution. But, as soon as all the base has reacted, the equilibrium between HA and  $\text{A}^-$  is reestablished by further ionization of the weak acid. Because some of the conjugate base is already present, less of the HA will ionize, so less free  $\text{H}^+$  is in solution at equilibrium, resulting in a higher (more basic) pH. Because the  $K_a$  has not changed, the extent of the ionization of HA is dictated by the ratio of concentrations of conjugate base to unionized acid,  $[\text{A}^-]/[\text{HA}]$ , because

$$\frac{K_a}{[\text{H}^+]} = \frac{[\text{A}^-]}{[\text{HA}]}$$



This explains why the pH of the solution becomes more basic throughout the titration even as there is unreacted acid in solution.

Remember, there are three important points on a titration curve:

- *The point when no base has been added.* The pH at this point represents the pH of a weak acid solution.
- *The half-equivalence point.* For a monoprotic acid, this point is the pH when half of the acid has been neutralized.
- *The equivalence point.* This is the point where the stoichiometric amount of base has been added to react with all ionizable protons in the acid.

## MATERIALS

- |                              |   |
|------------------------------|---|
| ➤ pH meter                   | ➤ ring stand                              |
| ➤ standardized NaOH solution | ➤ microstir bar ( <i>see Appendix C</i> ) |
| ➤ acetic acid solution       | ➤ magnetic stirrer                        |
| ➤ 100-mL beaker              | ➤ volumetric pipet                        |
| ➤ 50-mL buret                | (25-mL or combination of others)          |
| ➤ pipet bulb                 | ➤ buret clamp                             |
| ➤ pH standards               | ➤ clamp                                   |
| (pH=4.00 and pH=10.00)       | ➤ distilled water (in squirt bottle)      |

## PROCEDURE

In this section of the lab you will titrate a variety of weak acids with a standardized solution of a strong base. You will collect the titration data of solution pH as a function of volume of strong base added, and this curve will then be analyzed to determine the concentration of the weak acid and its ionization constant(s),  $K_a(s)$ , which will be compared to the literature value(s).

**Step A** Calibrate the pH meter. Your instructor will give you specific instructions.

**Step B** Rinse the pH meter tip with distilled water and pat dry with a paper towel.

**Step C** Prepare the buret by rinsing it with NaOH solution and removing any air bubbles from the tip.

**Step D** Fill the buret to 0.00 mL mark.

**Step E** Measure 15.00 mL of acetic acid solution, using a volumetric pipet, then place in a 100-mL beaker along with a microstir bar.

**Step F** Place the pH meter in solution and wait for the pH reading to be constant.

**Step G** Record the pH when 0.00 mL NaOH is added.

**Step H** Add 1–2 mL of NaOH and allow the solutions to mix thoroughly for one minute.

**Step I** Record pH when the reading has stabilized, and enter the exact volume of base added (to 0.01 mL).

**Step J** Repeat steps H and I. *Be sure to record total volume of base added, not the amount of NaOH added after last recorded volume.*

**Step K** Repeat until \_\_\_\_\_ mL of base has been added. *Add smaller, incremental volumes of NaOH as the pH reading approaches 6.0.* Continue to do so until change in pH decreases per volume of NaOH added.

**Step L** Finally, the pH of the resulting solution will not change appreciably after more base is added. At this point, the pH reading will be very constant for four consecutive volumes of base added. Stop. You have completed the titration.

### Calculations (Method III)

You are now ready to analyze your titration curves. Your instructor will tell you which method(s) to use in the analysis.

1. How many ionizable protons does your acid contain?
2. Determine the equivalence point(s) following these methods:
  - a. Use circles to determine the *change in concavity* of the transition region of the titration curve. The point when the concavity changes is the equivalence point.
  - b. Draw a best-fit line by hand using as many points as possible on the titration curves in the regions where there is not much change in pH (these lines are roughly horizontal). Exactly how many points these lines include depends on the number of data points in these regions. However, by moving a straightedge on these regions, you will find the lines that contain the greatest number of your data points. Then draw a line through as many points as possible in the transition region where the rate of change in pH is extremely great. Find the midpoint of this vertical line (where the pH changes rapidly) between the two points where it intersects the horizontal lines (where the pH changes slowly). Drop a perpendicular to the  $x$ -axis from the midpoint. This will give you the volume needed to reach this equivalence point.
  - c. Use the right angle method: taking a T-square or something else with a true right angle, slide it along the  $x$ -axis until the curve goes vertical. This will be the equivalence point since it is the steepest part of the curve.
  - d. Take the first and second derivatives of the titration curve data using a calculator or computer. Graph the first derivative data and the second derivative data. The peak(s) of the first derivative data, where the slope changes from positive to negative, is (are) equivalence point(s). The equivalence point(s) on the second derivative graph is (are) where the graph crosses the  $x$ -axis.
3. Use the equivalence point to determine the  $K_a$  of the acid.
4. Which acid/base indicator would you choose to show the endpoint of the titration of each acid? Explain your choice thoroughly.

### Post-Lab Questions

Predict how the calculated concentration of an acid would be affected—too high, too low, or not affected—by the following laboratory procedures. *Thoroughly explain* your answers.

1. The buret, after rinsing with distilled water, is filled with standardized hydroxide solution; the acid solution is immediately titrated to the endpoint.
2. An air bubble passes unnoticed through the tip of the buret during the titration.